

Approximation properties of basis functions in variational tree body problem*

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Abstract

A new variational basis with well-behaved local approximation properties and multiple output is proposed for Coulomb systems. The trial function has proper behaviour at all Coulomb centres. Nonlinear asymptotic parameters are introduced softly: they do not destroy the self-optimized local behaviour of the wave function at vanishing interparticle distances. The diagonalization of the Hamiltonian on a finite Hilbert subspace gives a number of meaningful eigenvalues. Thus together with the ground state some excited states are also reliably approximated. For three-body systems all matrix elements are analytically obtainable up to rational functions of asymptotic parameters. The feasibility of the new basis usage has been proved by a pilot computer algebra calculation. The negative sign of an electron pair local energy at their Coulomb centre has been revealed.

PACS number: 31.15.Pf

1 Introduction

In variational methods the required energy eigenvalue is obtained by averaging the Hamiltonian, or, in other terms, by averaging the local energy, defined by action of the Hamiltonian operator on a trial wave function. The

*Talk given at the International Conference "Quantization, Gauge Theory, and Strings" dedicated to the memory of Professor Efim Fradkin. Moscow. 5 – 10 May 2000. To be published in the Conference Proceedings.

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very variability of the local energy is a direct consequence of unavoidable approximate character of any chosen variational wave function. As a result, the global (averaged) quantities are much better reproduced in variational calculations than the local ones. Moreover, in practical calculations, the local reliability may be sacrificed in favour of faster convergence to the global values sought for. The known notion of the effective charge $Z^* = Z - 5/16$ in a two-electron atom (ion) is a good example of such sacrifice, since the local behaviour of an exact wave function in the Coulomb centre is determined by Z unscreened but not by Z^* .

The good local approximation quality of a variational wave function is a highly desirable goal since the problem onset (*Criteria of goodness for approximate wave functions* [1]) up until the present (*Quality of variational trial states* [2]). For any Coulomb system this quality is extremely vulnerable at the Coulomb singularity points. Without special care the local energy infinities take place at the Coulomb singularities, destroying the desired picture of the uniform approximation [3]. Luckily, the average Hamiltonian values are rather insensitive to these local infinities due to: (1) much higher degree of smallness of the neighbouring integrated volume ($\sim r^3$) in comparison with the degree of the Coulomb singularity ($\sim r^{-1}$) and (2) neutralizing of contributions with different signs at different points, as in customary cases of an effective charge or scale factor introduction.

In spite of great achievements of modern variational calculations in finding high precision energy values [4, 5, 6], the problem of the reliable local approximation of the wave functions persists. From now onwards, for brevity, the attribute “local” will be related only to the Coulomb centres vicinities. The Kato cusp conditions [7] can be imposed as a supplementary condition for mean energy minimum, thus introducing conditional extremum technique, usually more laborious. The method not affecting variational freedom and, nevertheless, avoiding local energy infinities was proposed earlier in [8]. The development of this method, presented below, adds the possibility to reproduce both local and asymptotic properties of an exact solution in the basis functions, thus striving for better uniformity of the wave function approximation.

2 Coulomb Variational Basis with Both Local and Asymptotic Proper Behaviour

The mentioned local behaviour of a many-body wave function is, in essence, that of some superposition of Coulomb solutions for the corresponding pair of particles. In the case of an isolated Coulomb pair, the wave function is a well-known product of a normalization factor, radial, and angular functions:

$$\psi = N R(\rho) Y(\mathbf{n}); \quad \rho = -\frac{Z_1 Z_2 e^2 m_1 m_2}{\hbar^2(m_1 + m_2)} |\mathbf{r}_1 - \mathbf{r}_2|, \quad \mathbf{n} = \frac{\mathbf{r}_1 - \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|},$$

$$R(\rho) = \exp(-\rho/n) \rho^l \Phi(1 + l - n, 2 + 2l; 2\rho/n). \quad (1)$$

The standard angular functions $Y(\mathbf{n})$ can be equivalently represented as symmetric irreducible tensors of the rank l , composed from the Cartesian projections of the unit vector \mathbf{n} and Kronecker's deltas:

$$l = 0, Y = 1; \quad l = 1, Y_i = n_i; \quad l = 2, Y_{ij} = 3 n_i n_j - \delta_{ij};$$

$$l = 3, Y_{ijk} = 5 n_i n_j n_k - \delta_{ij} n_k - \delta_{ik} n_j - \delta_{jk} n_i; \dots \quad (2)$$

The written Coulomb solution will be used not only for attracting pairs, when it leads to the discrete spectrum of bound states, but also for repulsing pairs. In the latter case the sequence of integral principal quantum numbers n gives the corresponding sequence of the Hamiltonian discrete "eigenvalues". They are not physically meaningful for isolated pairs: the "eigenfunctions" grow exponentially and are not normalizable. For repulsive pairs, which are embedded in a bound system, the negative Hamiltonian "eigenvalues" acquire the meaning of their local energies near the Coulomb centre, as the exponential growth of the "eigenfunctions" will be damped by the environment.

All products of the Coulomb wave functions of all pairs, attracting and repulsing as well, can constitute the variational basis [8]. A necessary contraction on dumb indices and selection of admissible asymptotics are implied. The permutation symmetry of identical particles should be imposed on the final form of the basis.

Such a basis, put in order by integer principal and orbital quantum numbers of different pairs, is full enough to approximate any analytical many-body wave function. The Kato cusp conditions are rigorously satisfied by the basis functions themselves. We stress the point that any approximate

fulfillment of the Kato cusp conditions leaves the difficulty of local energy infinities unsettled, no matter what precision of averaged quantities has been achieved.

For any pair of particles from a many-body system only a density matrix can be attributed and not a wave function. In the density matrix, unlike in the wave function of an isolated pair, the local and asymptotic parameters cannot remain identical. In order to reproduce in the basis functions this density matrix property we modify the Coulomb radial functions so as to allow independent adjustment of local and asymptotic variational parameters. The modified radial function $R(a, \rho)$ is defined as the product of the exponential factor $\exp(-a \rho)$ and a finite segment of the Maclaurin expansion of the ratio of the unmodified function $R(\rho)$ to the same exponential factor. The modified function has two adjustable parameters: a for the asymptotic behaviour, and n , real or imaginary, for the local behaviour near the Coulomb centre. This local behaviour is not affected by the performed soft introduction of the independent asymptotic behaviour, which is not connected with that of a confluent hypergeometric function. The Maclaurin series of $\exp(a \rho) R(\rho)$ up to ρ^{1+l+2k} appears to be the Laurent series in inverse even powers of n up to n^{-2k} . Just so the modified function has also the rearranged form:

$$R(a, \rho) = \sum_{k=0}^{k_{max}} \frac{c_k(a, \rho)}{n^{2k}}. \quad (3)$$

The Laurent coefficients $c_k(a, \rho)$ are proposed as the new two-body constituents of the many-body variational basis. They are independent of n polynomials in both ρ and a with the common exponential factor $\exp(-a \rho)$. Along with stretching the basis set, the usage of $c_k(a, \rho)$ instead of $R(a, \rho)$ will absorb the nonlinear parameters n in easily obtainable coefficients of a linear superposition. The proposed basis has inseparable cluster structure and the variational wave function should terminate only at the end of a cluster. In case of three-body Coulomb systems both the Hamiltonian and unity matrix elements can be computed analytically up to rational functions of all asymptotic parameters a .

The squares of effective principal quantum numbers of all attractive and repulsive Coulomb pairs, being included in the superposition coefficients, are tuned automatically with the latters. So the proposed basis produces the multiple output: not only the lowest root of the secular equation has the physical meaning, but some higher roots are also meaningful. Still a

majority of higher roots remains a mathematical artefact, hence, from the physical point of view, the Hamiltonian diagonalizes only partially.

3 Computer Algebra Feasibility of the New Method

The pilot computation confirms the possibility of cooperative treatment of several lowest states. With a relatively short wave function containing 54 terms (49 terms in the antisymmetric case) the helium para-S and ortho-S energy levels have been calculated in one run as:

para-S levels: -2.902900, -2.145871, -2.055637;

ortho-S levels: -2.175026, -2.068634, -2.036463,

while the results of high precision calculations given in [4] are:

para-S levels: -2.903724377033982, -2.145974046054634, -2.06127198974091;

ortho-S levels: -2.175229378237014, -2.068689067472468, -2.03651208309830.

Though these pilot numerical results are far from the record accuracy, they have definitely established the negative sign of the electron pair local energy in the Helium atom. This phenomenon can be tested experimentally in, *e. g.*, the Helium double ionization. The universal *Mathematica* program *vSlevels* is available upon request from the author.

In our approach interparticle (Hylleraas) variables are used for the basis formation, that is natural for elimination of the local energy infinities, and perimetric (Heron) variables — on the stage of analytical evaluation of integrals, that simplifies calculations. In hyperspherical variables the local energy infinities' problem appears more intricate. It has been solved principally through frame transformations in the recent work [9].

Acknowledgments

The author would like to thank V. B. Belyaev, B. V. Geshkenbein, L. B. Okun', V. S. Popov, and Yu. A. Simonov for constructive discussions and valuable comments.

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